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(54) Title: WATER-RESISTANT ADHESIVE

(57) Abstract: A water-resistant lightweight adhesive, particularly for use as a tile adhesive or grout, is produced by the addition of an adhesion promoter plus hollow filler and/or micro-spheres to an aqueous organic binding agent comprising a particular acrylic ester as an aqueous dispersion.

WATER-RESISTANT ADHESIVE

The present invention relates to a water-resistant, and preferably lightweight, adhesive that is particularly useful for fixing ceramic and other tiles, especially to vertical surfaces.

Many types of adhesive exist, and the properties required of them vary considerably depending upon the use to which they are to be put. Clearly adhesive strength to the intended substrate is important, and considerable effort is expended in adhesives development in combining satisfactory adhesive strength with other properties which allow the adhesive to be used in the way desired. Properties of the adhesive must be considered for storage, for application, and for performance during service life. An adhesive must have a reasonable shelf-life, it must be easy to apply, and it must retain its adhesive properties during service where it may be subjected to moisture or humidity and to various other environmental stresses and also to mechanical stresses. Such moisture and humidity resistance is clearly required in showers and bathrooms etc. Water-resistant adhesives are known in British Standard BS 5980:1980 as Class AA adhesives.

For certain adhesives a further consideration is of great significance. Some adhesives do not merely provide an adhesive bond line of no significant thickness, but rather provide some filling to fill irregularities in the substrates to be bonded together. Thus, a considerable volume of adhesive may be required. This is particularly true in the case of tile adhesives, especially ceramic tile adhesives. These adhesives provide a bond between rigid, often brittle, substrates that frequently have a rough surface and are not manufactured to tight tolerances. Part of the function of the adhesive therefore is to fill any surface irregularities. This

requirement for a certain thickness of adhesive is of course well recognised in the art. British Standard BS5980:1980, for example, refers to thin-bed and thick-bed fixing. Its successor, EN 12004, may also be noted. Even in the case of thin-bed fixing, adhesive layers of up to 3mm are used, and in the case of thick-bed fixing, adhesive thicknesses range from 3mm to 12mm. In practice, of course, tile adhesives will frequently be used at considerably greater thicknesses than are specified in that British Standard. The use of adhesives in such thick layers puts additional requirements on the properties of the adhesives. Cohesive strength and flexibility may become more important. In addition to such properties there is the important practical consideration of weight. Very large volumes of such adhesives are required for anything but the smallest job. Large volumes result in heavy weights which result in difficulties in transport and handling, and in extreme cases can lead to adhesive slump between application and setting.

Unfortunately, the two principal properties referred to above tend to work against one another. Water-resistant tile adhesives of high density are available, but it has proved extremely difficult to produce a light weight, water-resistant adhesive.

The present invention addresses this concern. The problem is to produce an adhesive, particularly suitable as a tile adhesive, and preferably of reduced specific gravity, that has suitable water-resistance without significantly impairing the other properties required of such adhesives. We have found that the specific gravity of an adhesive can be reduced by the incorporation of hollow filler and/or micro-spheres and/or an air-entrainment agent, together with fibres where necessary to counteract the reduction in cohesive strength or other structural impairment that might otherwise result.

Furthermore, we have found that careful selection of the base polymer or binding agent can lead to the desired water-resistance.

A first embodiment of the invention therefore provides a composition suitable for use as a water-resistant tile adhesive (preferably one meeting BS 5980:1980 Class AA) or grout, comprising:

(a) an aqueous organic binding agent preferably as an aqueous dispersion and including a poly(acrylic ester) or copolymer thereof, particularly a copolymer comprising an acrylate and a methacrylate;

(b) filler and/or micro-spheres;

(c) an adhesion promoter, preferably a silane; and

(d) optionally fibres.

A second embodiment of the invention provides a composition suitable for use as a water-resistant tile adhesive (again, preferably one meeting BS 5980:1980 Class AA)or grout, comprising: an aqueous organic binding agent preferably as an aqueous dispersion and comprising a copolymer comprising an acrylate and a methacrylate; an adhesion promoter, preferably a silane; and sufficient filler and/or micro- spheres to result in a specific gravity of the composition of less than 1 g/cm^3, and preferably less than 0.75g/cm^3; and preferably also fibres.

In a third embodiment the invention provides for the use of a copolymer comprising an acrylate and a methacrylate as an organic binding agent in a tile adhesive or grout containing filler and/or micro-spheres and as a means of increasing water-resistance.

The filler and/or microspheres are preferably hollow.

The binding agent preferably comprises a copolymer comprising an acrylate and a methacrylate, although other comparable repeat units may be provided instead or in addition. Preferably at least 70 mol %, especially at least 85 mol%, particularly at least 95 mol % and most particularly substantially all of the polymer is made up of acrylate and methacrylate repeat units. The copolymer preferably comprises 40-60 mol%, especially 45-55 mol% of each of the acrylate and the methacrylate. More than one type of acrylate and more than one type of methacrylate may be present, although at present it is preferred at least 75 mol% and preferably at least 85 mol% of each of the acrylate and methacrylate be of a single type. In particular, it is preferred that the acrylate be 2-ethyl hexyl acrylate and/or butyl acrylate (and if both preferably a minor quantity, say less than 10 mol%, of the latter), and that the methacrylate be methyl methacrylate and/or butyl methacrylate (and if both preferably a minor quantity, say less than 10 mol%, of the latter).

Other components may be present in the binding agent. For example acrylic acid and/or methacrylic acid may be present. The preferred amount of the total of these two materials is less than 5, particularly less than 1.5, for example 0.5-5, especially 0.75-1.5, say about 1, mol % based on the number of moles of acrylate and methacrylate in the copolymer.

The binding agent may also include, in addition to a base polymer (preferably that referred to above) one or more of the following:

(a) a coalescing solvent, such as a glycol ether for example 2 butoxy ethanol;

(b) an antifoaming agent for example a silicone; and

(c) surfactant which if present is preferably polymerizable or polymeric or otherwise becomes inactive once the adhesive or grout has been installed (polymeric compositions which contain such surfactants may be referred to as "surfactant free" since the surfactant is not available in the installed product).

The adhesion promoter is in general an important component of the composition. Its role in preferred compositions is to stabilize some form of association between the polymer of the binding agent and the substrate (tile or wall or other surface) and/or the filler. This will usually be by means of a simple chemical bond. In this way, adhesion is promoted. Preferred materials comprise silanes such as a β-glycidoxypropylmethyldiethoxy silane such as that marketed under the trade mark Witco Y15078. Preferred amounts are from 0.5-2% by weight based on the total weight of the composition.

Although the precise physical state of the adhesive will depend upon the exact end use, a consistency of a smooth paste is desirable. To this end, the binding agent preferably contains particles of "diameter" 0.01-1.0, particularly 0.05-0.5, especially about 0.1μm. The particles need not of course be precisely spherical, although they preferably are smooth having substantially no sharp edges, and may therefore be regarded as preferably substantially spherical. Where we refer to a diameter, we refer to the diameter of spherical particles of the same volume as the actual particles. The particle size distribution is not critical, but we prefer that at least 50%, more preferably at least 75%, especially at least 90%, and usually substantially all, of the particles are within the diameters ranges given above.

The binding agent (together with the other component if appropriate) preferably gives the overall composition a pH of 7-9. The binding agent preferably has good UV resistance and good cement resistance, in addition to the good water resistance for which is was primarily selected.

Furthermore, the binding agent preferably comprises a material having a minimum film forming temperature of 10°C or less, especially 5°C or less, for example about 3°C. The binding agent preferably has a glass transition temperature (Tg) of less than room temperature, more preferably 9 to 17°C, especially 11 to 15°C and most especially about 13°C.

At present, a preferred binding agent is an ionic aqueous emulsion marketed by Rhodia under the trademark Rhoximat DEC 27.

The adhesive is particularly useful for bonding ceramic tiles, and also for attaching tiles to vertical surfaces. It may also be used as a grout. We prefer, as mentioned above, that the adhesive conform to British Standard BS 5980:1980 Class AA and/or to EN 12004. In particular, we prefer that the adhesive be a Type 2 adhesive. Type 2 adhesives are manufactured as ready-for-use mixtures, and they consist of organic binding agents as an aqueous emulsion or latex, generally with mineral filling materials. The following organic binding agents may be used in addition to or in place of the ones mentioned above: one or more homo- or co-polymers of acrylic acid, methacrylic acid, acrylamide, methacrylic esters, vinyl esters, itaconic esters, vinyl ethers, olefins such as ethylene, styrene, butadiene, acrylonitrile or vinylidene chloride. By such homo- or co-polymers we include carboxylated versions of the basic polymers, such as carboxylated styrene butadiene acrylonitrile. Acrylic or

styrene acrylate co-polymers are preferred for some uses.

In order to reduce the specific gravity of the present adhesive, we prefer that the amount of conventional particulate inorganic fillers be kept to a minimum. Most preferably, we prefer that such fillers be substantially absent from the adhesive. A preferred maximum amount of such fillers may be taken as 30% by weight based on the total weight of the composition. A more preferred maximum is 10% by weight.

The micro-spheres may comprise any suitable material, the most important characteristic being their specific gravity. The micro-spheres will, in general, be hollow (in which case they may then constitute said hollow filler), and preferably closed. They will thus trap within them air or other generally inert gas depending on their method of formation. The term "micro-spheres" is well-known, and it will be appreciated that their shape need not be precisely spherical in a mathematical sense. Hollow filler of tubular or ellipsoidal shape may be used. Their size is not critical although we prefer they be sufficiently small that the texture of the adhesive is not adversely effected, and that they be sufficiently small in relation to their wall thickness that they be resistant to crushing during manufacture, use and service life of the adhesive. All of the micro-spheres present in any given sample of adhesive need not, of course, be of identical size. We prefer that the average diameter of the micro-spheres be from 10 to 500 microns; and we prefer that at least 50% preferably at least 75%, especially at least 90%, and most preferably substantially all, of the micro-spheres be within that range. Where the micro-spheres or hollow filler are not spherical, one may take as their diameter the diameter of a sphere of identical volume.

The material from which the micro-spheres are made may be selected from a wide variety of possibilities, thermoplastic polymers, glasses and ceramics all being acceptable. We have found borosilicate, particularly soda lime borosilicate, glass shells in the form of bubbles or beads to be particularly suitable as the micro-spheres. Those marketed under the trademark "Scotchlite" are preferred, but a product marketed under the trade mark "Expancel", which is made from a thermoplastic polymer encapsulating a gas may also be useful. Particularly preferred versions are known by the trademarks "Scotchlite K1" and "Expancel 551 WE".

We have found that a considerable volume of such micro-spheres can be combined with an organic binding agent to form an aqueous dispersion to provide a composition having the physical properties desired of a tile adhesive. Due to the very low specific gravity of the micro-spheres, the overall specific gravity of the composition is considerably reduced. For many purposes up to 40% by weight, generally from 10 to 40% by weight of micro-spheres may be provided based on the total weight of solids in the composition. Design of adhesives is inevitably a compromise, and as the content of micro-spheres increases the structural properties of the composition are likely to deteriorate somewhat. It is surprising, however, that significant reductions in specific gravity can be achieved at such little cost to these structural properties. Nonetheless, where very large additions of micro-spheres are desirable, or where some property such as cohesive strength, elongation or modulus is critical, we prefer that a certain quantity of fibre be added to the composition. In this way, we are able to compensate for any deleterious effect that the substitution of micro-spheres for conventional inorganic fillers may otherwise cause. A variety of types of fibre, organic or inorganic, may

be used. An example of inorganic fibres includes silica whiskers. However, we prefer organic fibres, such as cellulose, polyacrylonitrile and polyethylene. The length, thickness, size distribution and overall amount of the fibres will depend on exactly which physical properties of the composition are most important. For example, if a smooth, deformable, adhesive is required, possibly to allow flow into small cavities, then a lower loading of smaller fibres may be preferred. In general, however, a weight range, based on the total weight of the composition, of from 1 to 20% especially from 2 to 10%, may be taken as typical. Preferred fibres are those of length between 50 and 1500 microns, and we prefer that 50% of the fibres be in that range, more preferably that at least 75% by weight of the fibres have lengths from 100 to 1000 microns.

The reduction in specific gravity brought about by the incorporation of micro-spheres and/or hollow filler may be supplemented by air entrainment by other means. To this end the composition may include an air-entrainment agent, which serves to stabilise a froth-like or foam-like characteristic of the adhesive composition. Suitable air entrainment agents include soaps, emulsifying or foaming agents, which may act by forming a binding network in bubble walls. Examples include fatty acid ether sulfates, aliphatic carboxylic acid derivatives, and alkyl phenol ethoxylate.

A further useful component is a coalescing solvent which acts to reduce the ambient temperature at which the adhesive composition forms a film. Suitable coalescing solvents include butyl diglycol acetate, di-isobutyl glutarate, and ethylene glycol. The amount of the coalescing solvent is preferably from 0.5 to 6%, more preferably 1 to 2%, by weight based on the total weight of the composition. In general, the

amount required will depend upon the amount and nature of the organic binding agent.

Various other additives may be provided in the adhesive composition, some of the more important of which may be mentioned.

Preferred compositions of the invention may be classified as dispersion adhesives since they are based on organic binding materials in the form for example of aqueous emulsions or latexes. In some circumstances, however, aqueous solutions may be used. In any case, water will be present. The amount of water will usually be more than 20%, particularly more than 40% and often more than 50% by weight based on the total weight of the composition. Nonetheless, a solids content of from 10 to 60 percent based on the total weight of the composition will usually produce good results. The composition may be manufactured by mixing together various components, some of which are themselves emulsions, dispersions or solutions. The percentages of water just quoted of course include water added as such during manufacture and water added as part of such other components.

The structural characteristics of the adhesive composition may be improved, not only by the addition of the fibres, but also by the addition of one or more swelling clay minerals. In particular, swelling clay minerals may reduce or prevent slip. These minerals should be homogeneously distributed throughout the composition. As a result, structure is improved by thickening the composition. The clay may be of synthetic or natural origin and may exhibit a wide range of swelling ability. Preferred materials are smectite minerals such as montmorillonite when in calcium or magnesium form, or hectorite or laponite when in sodium form. Alternative

swelling clays are attapulgite and sepiolite. The quantity of swelling clay thickener is preferably at least 0.2 and more preferably at least 0.5%, and is preferably less than 10%, more preferably less than 5%, based on the total weight of the composition. The amount added will depend in part on the swelling ability of the clay. Additional thickeners may be added such as polyacrylic acid polymers and/or cellulose thickeners, examples of which include methyl hydroxy propyl cellulose, carboxy methyl cellulose and ethyl hydroxy cellulose. The preferred amount of such thickeners is from 0.1 to 5% by weight based on the total weight of the composition.

A cationic scavenger may be added in order to reduce or to prevent thickening of the adhesive composition during storage. A suitable cationic scavenger is a phosphate material, for example sodium hexametaphosphate.

Various other additives may be provided depending upon the precise use of the composition. For example, one may include one or more fungicides, one or more pigments, one or more dispersants, one or more cross-linking agents for the copolymer of the binding agent, silica, and other additives conventionally used in the adhesives industry.

The invention will now be further illustrated by the following examples. In these examples adhesives were prepared suitable for use as tile adhesives, and all were found to have excellent water-resistance. Examples 1 and 3 met the requirements of Class AA of BS 5980:1980.

This standard is not mandatory, and even adhesives exhibiting lower adhesive strength than that specified in the standard could nonetheless be useful for many applications.

In each case the compositions have an appearance of a mousse and were suitable for application to a vertical surface at a thickness of 0.5 cm without slump. In general, all examples showed excellent viscosity, low density, non-slip capability, flexibility and wetting character.

Example 1

An adhesive composition was prepared from the following components. The trade names for each component listed are explained below.

	% by weight
Water	49.28
Dispex G40	0.79
Acticide BX	0.21
Acticide BW	0.21
Butyl Diglycol Acetate	1.27
Carbopol EZ1	0.79
Bermocoll E481FQ	0.24
Attagel 30	0.53
AMP 95	0.31
Arbocel B400	2.36
Rhoximat Dec 27	34.29
Witco Y15078	1.02
Scotchlite K1	8.70

Performance

B.S.5980
Shear

14 days at rt (room temperature)	= 9.60 kN	(requirement 8.90 kN)
7 days at rt + 7 days at 100°C	= 6.70 kN	(requirement 4.50 kN)
7 days at rt + 7 days water immersion at rt	= 5.15 kN	(requirement 4.50 kN)

Tensile

14 days at rt	= 1.48 kN	(requirement 0.95 kN)
7 days at rt + 7 days water immersion at rt	= 1.21 kN	(requirement 0.56 kN)
14 days at rt after 20 min open time	= 1.60 kN	(requirement 0.95 kN)
14 days at rt after 5 min adjustability time	= 1.26 kN	(requirement 0.73 kN)
14 days at rt after 10 min adjustability time	= 1.52 kN	(requirement 0.45 kN)

EN 12004

14 days at rt	= 1.17 N/mm²	(requirement 1.0 N/mm²)
7 days at rt + 7 days water immersion at rt	= 0.514 N/mm²	(requirement 0.5 N/mm²)
14 days at rt + 14 days at 70°C + 24h at rt	= 1.27 N/mm²	(requirement 1.0 N/mm²)

Relative density	=	0.587
pH	=	7.75

This adhesive can be seen therefore to have satisfied standard BS 5980:1980 for Type 2 Class B and Class AA.

The standard EN 12004 is at present provisional. The adhesive of this example performs very similar to the requirements under that standard too.

Example 2

An adhesive composition was prepared from the following components.

	% by weight
Water	35.18
Dispex G40	0.77
Acticide BX	0.21
Acticide DW	0.21
Butyl Diglycol Acetate	1.23
50% Calgon PT solution	0.31
Carbopol EZ1	0.77
Bermocoll E481FQ	0.46
Attagel 30	0.64
AMP 95	0.31
Arbocel B400	4.60
Rhoximat Dec 27	33.44
Perlankrol ESK32	0.31
Witco Y15078	0.99
Expancel 551 WE	20.57

Performance

B.S. 5980

Shear

14 days at rt	= 12.29 kN	(requirement 8.90 kN)
7 days at rt + 7 days at 100°C	= 5.32 kN	(requirement 4.50 kN)
7 days at rt + 7 days water immersion at rt	= 3.51 kN	(requirement 4.50 kN)

EN 12004

14 days at rt	= 1.162 N/mm²	(requirement 1.0 N/mm²)
7 days at rt + 7 days water immersion at rt	= 0.310 N/mm²	(requirement 0.5 N/mm²)
14 days at rt + 14 days at 70°C + 24h at rt	= 1.124 N/mm²	(requirement 1.0 N/mm²)
14 days at rt + 14 days at 70°C	= 0.789 N/mm²	(requirement 1.0 N/mm²)

Relative density	=	0.500
pH	=	5.92

This adhesive satisfied Standard BS 5980:1980 for Type 2 Class B. Water-resistance was good, being superior to prior art adhesives of low weight, but it was slightly inferior to that required for Class AA. The adhesive can also be seen to perform reasonably well against EN 12004.

Example 3

An adhesive composition was prepared from the following components.

	% by weight
Water	49.59
Dispex G40	0.80
Acticide BX	0.21
Acticide DW	0.21
Butyl Diglycol Acetate	0.64
Carbopol EZ1	0.80
Bermocoll E481FQ	0.24
Attagel 30	0.53
AMP 95	0.32
Arbocel B400	2.38
Rhoximat Dec 27	34.51
Witco Y15078	1.02
Scotchlite K1	4.78
Scotchlite K37	3.98

Performance

B.S. 5980
Shear

14 days at rt		= 14.58 kN(requirement 8.90 kN)
7 days at rt + 7 days at 100°C		= 8.10 kN (requirement 4.50 kN)
7 days at rt + 7 days water immersion at rt		= 4.92 kN (requirement 4.50 kN)
Relative density	=	0.660
pH	=	8.03

The adhesive satisfied BS 5980:1980 for Type 2 Class B and Class AA.

In the above Examples the materials identified by trade names have the following chemistry and function.

Trade name	Chemical Type	Function
Rhoximat DEC 27	An ionic aqueous emulsion of acrylic ester, 48% dispersion in water	Base polymer
Dispex G40	Sodium salt of carboxylated copolymer	Surfactant
Acticide BX	Preparation from N-formals and isothialozones	In-can biocide
Acticide DW	Preparation of 2-Octyl-2H-isothiazol-3-one	Dry film biocide
Carbopol EZ1	Poly acrylic acid	Thickener
Bermocoll E481FQ	High viscosity grade ethyl hydroxyethyl cellulose	Cellulosic thickener
AMP 95	2-amino-2-methyl-1-propenol	pH adjuster
Arbocel B400	Natural cellulose fibre	Fibre filler
Texicryl 13-038	Styrene acrylic copolymer (50% dispersion in water)	Base polymer
Butyl diglycol acetate	Butyl diglycol acetate	Coalescing solvent
Attagel 30	Hydrated magnesium aluminium silicate	Swelling clay
Perlankrol ESK-32	Fatty alcohol ether sulphate (sodium salt)	Air entrainer
Expancel 551 WE	Copolymer encapsulating a blowing agent	Lightweight filler
Scotchlite K1	Soda lime borosilicate glass bubbles	lightweight filler

Scotchlite K37	Soda lime borosilicate glass bubbles	Lightweight filler
Witco Y15078	β-Glycidoxy propyl methyldiethoxy silane	Adhesion promoter

Claims

1. A composition suitable for use as a water-resistant tile adhesive or grout, comprising:
   (a) an aqueous organic binding agent including a poly(acrylic ester) or copolymer thereof;
   (b) filler and/or micro-spheres;
   (c) an adhesion promoter; and
   (d) optionally fibres.

2. A composition suitable for use as a water-resistant tile adhesive or grout, comprising: an aqueous organic binding agent comprising a poly(acrylic ester) or copolymer thereof an adhesion promoter; and sufficient filler and/or micro-spheres to result in a specific gravity of the composition of less than 1 g/cm^3.

3. A composition according to any claim 1 or 2, in which the binding agent includes a copolymer of acrylate and methacrylate monomers.

4. A composition according to claim 3, in which the binding agent includes a copolymer comprising 2-ethyl hexyl acrylate and methyl methacrylate.

5. A composition according to any preceding claim, in which the binding agent additionally includes acrylic acid and/or methacrylic acid.

6. A composition according to any preceding claim, in which the adhesion promoter comprises a silane.

7. A composition according to any preceding claim, in

which the adhesion promoter forms a bond between the copolymer and the component (b) and/or between the copolymer and a tile or substrate to which a tile is to be attached.

8. A composition according to any preceding claim, in which the aqueous organic binding agent comprises an aqueous dispersion.

9. A composition according to claim 7, in which the micro-spheres comprise boro-silicate glass encapsulating a gas.

10. A composition according to any preceding claim, containing from 10 to 40 percent by weight of micro-spheres based on the total weight of solids in the composition.

11. A composition according to any preceding claim, containing from 1 to 20 percent by weight of fibres based on the total weight of the composition.

12. A composition according to any preceding claim, which contains less than 30 percent by weight of inorganic particulate filler based on the total weight of the composition.

13. A composition according to any preceding claim, containing from 10 to 60 percent solids based on the total weight of the composition.

14. A composition according to any preceding claim, containing at least 40% by weight of water based on the total weight of the composition.

15. A composition suitable for use as a water-resistant tile adhesive or grout, comprising:

(a) an aqueous organic binding agent;

(b) filler and/or microspheres;

(c) an adhesion promoter;

(d) a polymerizable surfactant; and

(e) optionally fibres.

16. The use of a copolymer comprising 2-ethyl hexyl acrylate and methyl methacrylate as an organic binding agent in a tile adhesive or grout containing hollow filler and/or micro-spheres and as a means of increasing water-resistance.

17. The use according to claim 16 in which the adhesive composition is a tile adhesive according to British Standard BS 5980:1980 class AA and/or to EN 12004.

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(54) Title: WATER-RESISTANT GROUT AND TITLE ADHESIVE COMPOSITION

(57) Abstract: A water-resistant lightweight adhesive, particularly for use as a tile adhesive or grout, is produced by the addition of an adhesion promoter plus hollow filler and/or micro-spheres to an aqueous organic binding agent comprising a particular acrylic ester as an aqueous dispersion.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K3/10 C09D5/34 C09J133/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K C09D C09J A55X

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 214 696 A (DSM RESINS BV) 18 March 1987 (1987-03-18) example 6 ---	1-3
X	EP 0 220 841 A (BEECHAM HOME IMPROV PROD INC) 6 May 1987 (1987-05-06) page 3, line 50 - line 55; claims; examples ---	1-3,6
X	EP 0 544 569 A (RHONE POULENC CHIMIE) 2 June 1993 (1993-06-02) claims 1,6; examples 2,6,17 ---	1,3,5-8
X	US 6 001 907 A (HUANG MISTY W) 14 December 1999 (1999-12-14) tables ---	1-3,5-8

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
23 October 2001	05/11/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schueler, D

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 199 921 A (POLYCHEMIE GMBH) 5 November 1986 (1986-11-05) claims 1,5,8; example 2	1,6,8
X	US 5 124 384 A (GOLDSTEIN JOEL E) 23 June 1992 (1992-06-23) the whole document	1,6,8
X	EP 0 857 772 A (WACKER CHEMIE GMBH) 12 August 1998 (1998-08-12) claims; examples 2,4,6-8	1,6,8
X	EP 0 924 250 A (WITCO CORP) 23 June 1999 (1999-06-23) table 1	1,6,8
A	WO 00 06611 A (STEPAN CO ;SIDDIQUI ADNAN (US); KLEINFELD ELAINE R (US); SCHULTZ A) 10 February 2000 (2000-02-10) claims 1,4,65,67-71,137	15
X	JP 11 189764 A (MITSUI CHEM INC) 13 July 1999 (1999-07-13) table 1	16
X	EP 0 256 144 A (NAT STARCH CHEM CORP) 24 February 1988 (1988-02-24) page 6, line 5 - line 23; examples 1,3,6	16
X	US 4 590 230 A (KAMADA KEIICHI ET AL) 20 May 1986 (1986-05-20) example 4	16
X A	column 4, line 27-43 column 4, line 44 - line 60	1,3-8 15
A	EP 0 502 573 A (DSM NV) 9 September 1992 (1992-09-09) page 3, line 28; claims; examples 1,2,5,6	16

INTERNATIONAL SEARCH REPORT

Inter nal application No.
rCT/GB 01/01671

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

As a result of the prior review under R. 40.2(e) PCT,
no additional fees are to be refunded.

1. [X] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[X] The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-14

   A composition characterised by a) an acrylic resin, b) a filler and c) an adhesion increasing agent.

2. Claim : 15

   A composition characterised by a) a resin, b) a filler, c) an adhesion increasing agent and d) a polymerizable surfactant; the definition for the resin being broader than in subject 1;

3. Claims: 16-17

   A grout or tile adhesive composition comprising a copolymer of ethylhexyl acrylate and methyl methacrylate; free of adhesion improving agent, filler or surfactant.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0214696 A	18-03-1987	NL 8502463 A	01-04-1987
		AT 53398 T	15-06-1990
		CA 1303279 A1	09-06-1992
		DE 3671756 D1	12-07-1990
		EP 0214696 A1	18-03-1987
		ES 2001297 A6	01-05-1988
		PT 83351 A ,B	01-10-1986
		US 5100955 A	31-03-1992
EP 0220841 A	06-05-1987	US 4626567 A	02-12-1986
		AT 65255 T	15-08-1991
		AU 590632 B2	09-11-1989
		AU 6433186 A	30-04-1987
		CA 1294086 A1	07-01-1992
		DE 3680285 D1	22-08-1991
		EP 0220841 A2	06-05-1987
		NZ 218043 A	28-08-1990
EP 0544569 A	02-06-1993	FR 2684107 A1	28-05-1993
		EP 0544569 A1	02-06-1993
US 6001907 A	14-12-1999	BR 9805885 A	14-12-1999
		EP 0924250 A1	23-06-1999
		JP 11263967 A	28-09-1999
		SG 66503 A1	22-08-2000
EP 0199921 A	05-11-1986	DE 3512456 A1	09-10-1986
		EP 0199921 A2	05-11-1986
US 5124384 A	23-06-1992	NONE	
EP 0857772 A	12-08-1998	DE 19704553 A1	13-08-1998
		EP 0857772 A1	12-08-1998
		PL 324673 A1	17-08-1998
		US 6184274 B1	06-02-2001
EP 0924250 A	23-06-1999	BR 9805885 A	14-12-1999
		EP 0924250 A1	23-06-1999
		JP 11263967 A	28-09-1999
		SG 66503 A1	22-08-2000
		US 6001907 A	14-12-1999
WO 0006611 A	10-02-2000	AU 5460399 A	21-02-2000
		EP 1102794 A1	30-05-2001
		WO 0006611 A1	10-02-2000
JP 11189764 A	13-07-1999	NONE	
EP 0256144 A	24-02-1988	US 4710526 A	01-12-1987
		AU 571373 B2	14-04-1988
		AU 6005986 A	14-01-1988
		EP 0256144 A2	24-02-1988
		JP 61158851 A	18-07-1986
US 4590230 A	20-05-1986	JP 1859711 C	27-07-1994
		JP 5067674 B	27-09-1993
		JP 58152074 A	09-09-1983

Information on patent family members

International application No
PCT/GB 01/01671

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0502573 A	09-09-1992	NL 9100351 A	16-09-1992
		EP 0502573 A1	09-09-1992